

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D 17/06, 1/72	A1	(11) International Publication Number: WO 94/11488 (43) International Publication Date: 26 May 1994 (26.05.94)
(21) International Application Number: PCT/GB93/02346 (22) International Filing Date: 15 November 1993 (15.11.93) (30) Priority data: 9224014.2 16 November 1992 (16.11.92) GB 9226246.8 16 December 1992 (16.12.92) GB (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: CARTER, Malcolm, Nigel, Alan (deceased). HOUGHTON, Mark, Philip ; Berliozplein 1, NL-2651 VG Berkel en Rodenrijs (NL). HULL, Michael ; "Windcliffe", Alvanley Road, Helsby, Warrington, Cheshire WA6 9PS (GB).		(74) Agent: FORD, Michael, Frederick; Mewburn Ellis, 2 Cur-sitor Street, London EC4A 1BQ (GB). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DETERGENT COMPOSITIONS (57) Abstract <p>A particulate detergent composition of high bulk density has a surfactant system comprising an ethoxylated C₈-C₁₅ aliphatic alcohol nonionic surfactant of low ethoxylation (2-6) and a high degree of chain branching (at least 40 wt% based on the alcohol) and is substantially free of low-ethoxylated nonionic surfactant having a lesser degree of chain branching. The use of highly branched nonionic surfactant improves delivery of the composition to the wash in an automatic washing machine, and also gives detergency benefits.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

DETERGENT COMPOSITIONSTECHNICAL FIELD

The present invention relates to particulate detergent compositions containing nonionic surfactants. The invention is particularly concerned with particulate detergent compositions having high bulk density.

BACKGROUND AND PRIOR ART

Nonionic surfactants have beneficial cleaning characteristics when included in detergent formulations, as they are particularly effective in removing hydrophobic soils such as hydrocarbon oils, complex fats and other long-chain unsaturated and saturated glycerides.

However when particulate detergent compositions containing nonionic surfactants come in contact with aqueous solutions the nonionic surfactants tend to form viscous phases which impede delivery from the dispenser of an automatic washing machine or from a delivery device, and give poor dissolution and dispersion in the wash liquor. Nonionic surfactants having a low degree of ethoxylation, employed because of their oily soil detergency, are especially problematic in this respect.

In high bulk density powders the problem is exacerbated because the capillary diameter of the powder bed is smaller than in lower bulk density powders and water penetration is therefore slower. Delivery problems have also proved especially acute with powders containing water insoluble builders such as alkali metal aluminosilicates.

SUBSTITUTE SHEET

- It has now been discovered that the difficulty of producing a detergent powder containing ethoxylated alcohol nonionic surfactants and having good delivery and dissolution characteristics, without the need for any processing modifications, can be overcome by the use of highly-branched low-ethoxylate nonionic surfactants, and the exclusion of less branched materials of low degrees of ethoxylation. At the same time another benefit, of better detergency at low wash temperatures, is achieved.
- 10 Spray-dried phosphate-built detergent powders of conventional bulk density containing highly branched nonionic surfactants are disclosed in GB 1 560 076 (Procter & Gamble) and GB 2 020 688B (Unilever).
- 15 High bulk density detergent powders containing nonionic surfactants are described in the art, and lists of suitable nonionic surfactants for possible inclusion in such powders may include some highly branched materials, as for example in EP 513 824A (Kao), EP 342 043A (Procter & Gamble) and EP 364 881A (Henkel). However, no preference for branched
- 20 nonionic surfactants, or specific disclosure of their use, in high bulk density powder in the prior art is known.

- 3 -

DEFINITION OF THE INVENTION

The present invention accordingly provides a particulate detergent composition having a bulk density of at least 600 g/l and comprising a surfactant system comprising a
5 nonionic surfactant, at least one detergency builder and optionally other detergent ingredients, wherein the nonionic surfactant comprises a branched-chain nonionic surfactant which is an ethoxylated C₈-C₁₅ aliphatic alcohol having a degree of chain branching (defined herein as the weight% of
10 the alcohol constituted by branched material) of at least 40 wt%, and having an average degree of ethoxylation of from 2 to 6, and the surfactant system is substantially free of ethoxylated alcohol nonionic surfactants having a degree of chain branching of less than 40 wt% and a degree of
15 ethoxylation of from 2 to 6.

The invention further provides the use of a branched-chain nonionic surfactant which is an ethoxylated C₈-C₁₅ aliphatic alcohol having a degree of chain branching of at least 40 wt% (based on the alcohol) and having an average
20 degree of ethoxylation of from 2 to 6, to improve the solubility and/or rate of dissolution of a particulate detergent composition having a bulk density of at least 600 g/l.

SUBSTITUTE SHEET

DETAILED DESCRIPTION OF THE INVENTIONThe surfactant system

The detergent compositions of the invention are characterised by a surfactant system containing as an
5 essential ingredient a branched-chain nonionic surfactant having a low degree of ethoxylation.

As explained in more detail below, it is within the scope of the invention for further ethoxylated nonionic surfactants, outside the specifically excluded class defined above,
10 additionally to be present.

It is also within the scope of the invention for additional surfactants other than ethoxylated nonionic surfactants to be present.

The total amount of detergent-active material
15 (surfactant) in the compositions of the invention is suitably from 5 to 50 wt%. Of particular interest are high-performance compositions containing relatively high levels of surfactant, preferably from 10 to 50 wt% and more preferably from 15 to 50 wt%.

20 The branched-chain ethoxylated nonionic surfactant

The branched-chain nonionic surfactant has a degree of branching of at least 40 wt%, preferably at least 50 wt%. The degree of branching is defined here as the weight percentage of branched material (material containing any
25 branching in the molecule) in the parent alcohol of the ethoxylate. This may be determined, for example, by NMR or by gas chromatographic mass spectrometry. For commercial materials, the information is normally available from the manufacturer.

- 5 -

A degree of branching of up to 100 wt% is in principle acceptable, provided that no quaternary carbon atoms are present, but for environmental reasons a degree of branching not exceeding 70 wt% is generally preferred. A preferred
5 range for the degree of branching is from 45 to 70 wt%.

Preferably, from 20 to 50% of the carbon atoms (of the alcohol) are located on side chains. Side chains are defined as all chains other than the main chain, which is defined as the longest chain identifiable in the molecule.

10 The degree of ethoxylation of the branched-chain nonionic surfactant is from 2 to 6, preferably from 2.5 to 4.

It may be advantageous for the branched-chain nonionic surfactant to have an alkyl chain length of less than C_{12} , preferably from C_9 to $C_{11.5}$, as described and claimed in our
15 copending application of even date, claiming priority from British Patent Application No. 92 24014.2 filed on 16 November 1992. However, the benefits of the present invention are also observed with longer-chain materials.

20 It is preferred for the level of free alcohol in the nonionic surfactant to be less than 5 wt%, more preferably less than 1 wt%.

Branched-chain nonionic surfactants suitable for use in the present invention include the commercially available materials listed in Table 1. (* denotes Trade Mark).
25 Mixtures of these materials may also be used in order to achieve intermediate degrees of ethoxylation.

- 6 -

TABLE 1

	<u>Name</u>	<u>Manufr.</u>	<u>Chain</u> <u>length</u> (nominal)	<u>EO(av)</u> (average)	<u>Branching</u>
5	Lialet* 125-3	Enichem	C ₁₂₋₁₅	3	60% (C ₁₋₄)
	Lialet* 125-4	Enichem	C ₁₂₋₁₅	4	60% (C ₁₋₄)
	Lialet* 125-5	Enichem	C ₁₂₋₁₅	5	60% (C ₁₋₄)
	Lialet* 125-6	Enichem	C ₁₂₋₁₅	6	60% (C ₁₋₄)
	Lialet* 125 4-6	Enichem	C ₁₂₋₁₅	4-6	60% (C ₁₋₄)
10	Lialet* 111-3	Enichem	C ₁₁	3	47% (C ₁₋₄)
	Lialet* 111-4	Enichem	C ₁₁	4	47% (C ₁₋₄)
	Lialet* 111-5	Enichem	C ₁₁	5	47% (C ₁₋₄)
	Lialet* 111-6	Enichem	C ₁₁	6	47% (C ₁₋₄)
	Lialet* 111 4-6	Enichem	C ₁₁	4-6	47% (C ₁₋₄)
15	Lialet* 91 4-6	Enichem	C ₉₋₁₁	4-6	47% (C ₁₋₄)
	Synperonic* 91-4-6 ICI		C ₉₋₁₁	4-6	60% (C ₁)
	Genapol* GX-030	Hoechst	C ₁₃	3	90%
	Genapol* OX-030	Hoechst	C ₁₂₋₁₅	3	60%
20	Nemol* G23-3	Masso Ecarol	C ₁₂₋₁₃	3	60%

- 7 -

The chain distributions of some highly branched nonionic surfactants (weight percent based on the parent alcohol) preferably used in the compositions of the invention are given below.

5	<u>Lialet 125 series ex Enichem</u>		
10	C ₁₂ (20.8 wt%):	n-C ₁₂ (main chain)	10.5
		C ₁₁ 2-methyl	3.5
		C ₁₀ 2-ethyl	1.8
		C ₉ 2-propyl	1.9
		C ₈ 2-butyl and C ₇ 2-pentyl	3.1
15	C ₁₃ (30.4 wt%):	n-C ₁₃ (main chain)	11.2
		C ₁₂ 2-methyl	5.0
		C ₁₁ 2-ethyl	2.8
		C ₁₀ 2-propyl	3.3
		C ₉ 2-butyl	3.8
20	C ₁₄ (30.8 wt%):	n-C ₁₄ (main chain)	12.2
		C ₁₃ 2-methyl	4.4
		C ₁₂ 2-ethyl	2.5
		C ₁₁ 2-propyl	2.8
		C ₁₀ 2-butyl	3.4
25	C ₁₅ (17.7 wt%):	n-C ₁₅ (main chain)	5.8
		C ₁₄ 2-methyl	2.3
		C ₁₃ 2-ethyl	1.3
		C ₁₂ 2-propyl	1.6
		C ₁₁ 2-butyl	2.1
30	Total branched C ₁₂₋₁₅ :	C ₁₀ 2-pentyl	2.4
		C ₉ 2-hexyl	2.2
		60.00%	

SUBSTITUTE SHEET

Lialet 111 series ex Enichem

5	C ₁₁ (96.10%):	n-C ₁₁ (main chain)	49.2
		C ₁₀ 2-methyl	17.3
		C ₉ 2-ethyl	9.3
		C ₈ 2-propyl	9.7
		C ₇ 2-butyl and C ₆ 2-pentyl	10.6

Total branched material: 46.90%

Examples of low-ethoxylated nonionic surfactants outside the definition above include those listed in Table 2.

10

TABLE 2

15	Lorodac* LS 3L	DAC	C ₁₂₋₁₆	3	none
	Inbentin* 3	Kolb	C ₁₂₋₁₄	3	none
	Dobanol* 25-3	Shell	C ₁₂₋₁₅	3	25% (C ₁)
	Dobanol* 23-3	Shell	C ₁₂₋₁₃	3	25% (C ₁)
	Dobanol* 91-5	Shell	C ₉₋₁₁	5	25% (C ₁)
	Synperonic* A3	ICI	C ₁₂₋₁₅	3	48%
	Synperonic* A3X	ICI	C ₁₂₋₁₅	3	42%

Chain length distributions of some of these materials are given below.

- 9 -

Dobanol 25 series ex Shell

5	C ₁₂ (19.9 wt%):	n-C ₁₂ (main chain)	16.3
		C ₁₁ 2-methyl	1.9
		C ₁₀ 2-ethyl	0.8
		Other branched C ₁₂	0.9
10	C ₁₃ (31.2 wt%):	n-C ₁₃ (main chain)	23.4
		C ₁₂ 2-methyl	3.3
		C ₁₁ 2-ethyl	1.3
		C ₁₀ 2-propyl	0.8
		C ₉ 2-butyl	1.2
		C ₈ 2-pentyl	1.2
15	C ₁₄ (29.4 wt%):	n-C ₁₄ (main chain)	22.8
		C ₁₃ 2-methyl	2.6
		C ₁₂ 2-ethyl	1.1
		C ₁₁ 2-propyl	0.7
		C ₁₀ 2-butyl	0.9
		C ₉ 2-pentyl	1.3
20	C ₁₅ (19.1 wt%):	n-C ₁₅ (main chain)	14.0
		C ₁₄ 2-methyl	1.8
		C ₁₃ 2-ethyl	0.9
		C ₁₂ 2-propyl	0.5
		C ₁₁ 2-butyl	0.6
		Other branched C ₁₅	1.3
Total branched C ₁₂₋₁₅ material: 23.10%			

SUBSTITUTE SHEET

Dobanol 91 series ex Shell

	C ₈ (0.7%):	n-C ₈	0.7
	C ₉ (19.0%):	n-C ₉	17.5
		C ₈ 2-methyl	1.0
5		C ₇ 2-ethyl	0.3
		C ₆ 2-propyl	0.2
	C ₁₀ (45.8%):	n-C ₁₀	40.7
		C ₉ 2-methyl	2.9
		C ₈ 2-ethyl	1.0
10		other branched	1.2
	C ₁₁ (33.3%):	n-C ₁₁	25.5
		C ₁₀ 2-methyl	2.4
		C ₉ 2-ethyl	1.0
		Other branched	4.4
15	C ₁₂ (1.6%)	n-C ₁₂	0
		branched	1.6

Total branched C₈₋₁₂ material: 16.00%

Synperonic series ex ICI

	C ₁₃ (67.2%):	n-C ₁₃	44.0
20		C ₁₂ 2-methyl	11.9
		C ₁₁ 2-ethyl	3.8
		C ₁₀ 2-propyl	3.1
		C ₉ 2-butyl and	
		C ₈ 2-pentyl	4.4

- 11 -

5	C ₁₅ (35.1%):	n-C ₁₅	20.9
		C ₁₄ 2-methyl	2.4
		C ₁₃ 2-ethyl	1.0
		C ₁₂ 2-propyl	0.8
		C ₁₁ 2-butyl, C ₁₀ 2-pentyl, C ₉ 2-hexyl	2.4

Total branched material: 29.80%

More highly ethoxylated nonionic surfactants

As already indicated, low-ethoxylated (2-6EO) nonionic
 10 surfactants which are less highly branched are excluded from
 the compositions of the invention. Nonionic surfactants
 having a higher degree of ethoxylation may, however, be
 additionally present. This is advantageous from the point of
 view of detergency. These may be either highly branched (at
 15 least 40 wt%) or less highly branched (less than 40 wt%), the
 use of either being within the scope of the invention.

A preferred nonionic surfactant system in compositions of
 the invention therefore comprises:

(a) a branched-chain nonionic surfactant which is an
 20 ethoxylated C₈-C₁₅ aliphatic alcohol having a degree of chain
 branching of at least 40 wt% and having an average degree of
 ethoxylation of from 2 to 6, and

(b) a nonionic surfactant which is an ethoxylated C₈-C₁₅
 25 aliphatic alcohol having an average degree of ethoxylation of
 from 6.5 to 10, preferably from 6.5 to 8.

Examples of nonionic surfactants of higher ethoxylation
 and higher branching within the definition (b) which may be
 used in the compositions of the invention include the
 higher-ethoxylated analogues of the highly branched materials
 30 listed in Table 1 above, for example, Lialet 125-7.

SUBSTITUTE SHEET

Surprisingly, however, better powder dissolution may be observed when the more highly ethoxylated nonionic surfactant is less highly branched.

5 An advantageous nonionic surfactant system in compositions of the invention therefore comprises:

- (a) a branched-chain nonionic surfactant which is an ethoxylated C_8-C_{15} aliphatic alcohol having a degree of chain branching of at least 40 wt% and having an average degree of ethoxylation of from 2 to 6, and
- 10 (b) a nonionic surfactant which is an ethoxylated C_8-C_{15} aliphatic alcohol having a degree of chain branching of less than 40 wt% and having an average degree of ethoxylation of from 6.5 to 10, preferably from 6.5 to 8.

15 Examples of nonionic surfactants within the definition (b) include the higher-ethoxylated analogues of the less branched materials listed in Table 2 above, for example, Synperonic A7, Lorodac LS 7L, Dobanol 23-7, Dobanol 25-7.

20 Nonionic detergent-active compounds are suitably present in the compositions of the invention in a total amount of from 2 to 50 wt%, preferably from 5 to 30 wt%.

Other detergent-active compounds

25 As previously indicated, provided that nonionic surfactants of the class specifically excluded above are absent, other detergent-active materials may be present in the compositions of the invention.

Detergent-active material present other than the nonionic surfactants may be other anionic (soap or non-soap), cationic, zwitterionic, amphoteric, or any combination of these.

- 13 -

Anionic detergent-active compounds may be present in an amount of from 0 to 40 wt%, preferably from 0 to 20 wt%. It is preferred if the ratio of nonionic surfactant to anionic surfactant is within the range of 2:8 to 9:1.

5 Synthetic anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15} ; primary and secondary alkyl sulphates, particularly sodium $C_{12}-C_{15}$
10 primary alcohol sulphates, olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinate; and fatty acid ester sulphonates.

It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from
15 naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rapeseed oil.

Preferred surfactant systems

Especially preferred compositions in accordance with the
20 invention have surfactant systems consisting essentially of branched-chain ethoxylated nonionic surfactant as defined above in combination with linear alkylbenzene sulphonate (LAS) or primary alcohol sulphate (PAS) or both.

Surfactant systems of especial interest consist
25 essentially of

(i) from 40 to 100 wt% of the ethoxylated nonionic surfactant, and

(ii) from 0 to 60 wt% of linear alkylbenzene sulphonate and/or primary C_8-C_{18} alcohol sulphate.

SUBSTITUTE SHEET

Detergency builders

The detergent powders of the invention contain one or more detergency builders, suitably in an amount of from 5 to 80 wt%, preferably from 20 to 60 wt%.

- 5 The invention is especially applicable to compositions containing alkali metal aluminosilicates as builders.

- Alkali metal (preferably sodium) aluminosilicates may generally be incorporated in amounts of from 5 to 60% by weight (anhydrous basis) of the composition, preferably from
10 25 to 55 wt%, and suitably, in a heavy duty detergent composition, from 25 to 48 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:

- 15 $0.8-1.5 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 0.8-6 \text{ SiO}_2$

- These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the
20 crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

- Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in
25 GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders.

- 15 -

Alternatively, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal
5 aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to
10 aluminium ratio not exceeding 1.07. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Other builders may also be included in the detergent compositions of the invention if necessary or desired.

15 Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever). Organic builders that may be present include
20 polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and
25 alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Especially preferred supplementary builders are
30 polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%; and monomeric

SUBSTITUTE SHEET

polycarboxylates, more especially citric acid and its salts, suitably used in amounts of from 3 to 35 wt%, more preferably from 5 to 30 wt%.

Preferred compositions of the invention preferably do not contain more than 5 wt% of inorganic phosphate builders, and are desirably substantially free of phosphate builders.

The compositions in accordance with the invention may contain alkali metal, preferably sodium, carbonate, to increase detergency and to ease processing. Sodium carbonate may generally be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%, and most suitably from 2 to 13 wt%. However, compositions free of alkali metal carbonate are also within the scope of the invention.

Other ingredients

Fully formulated laundry detergent compositions in accordance with the present invention may additionally contain any suitable ingredients normally encountered, for example, inorganic salts such as sodium silicate or sodium sulphate; organic salts such as sodium citrate; antiredeposition aids such as cellulose derivatives and acrylate or acrylate/maleate polymers; fluorescers; bleaches, bleach precursors and bleach stabilisers; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; fabric softening compounds.

Processing and powder properties

The particulate detergent compositions of the invention may in principle be prepared by any of the available tower (spray-drying), non-tower (granulation) or combination processes.

- 17 -

Of especial interest are compositions of high bulk density - at least 600 g/l, preferably at least 700 g/l and more preferably at least 800 g/l - which may be prepared by granulation and/or densification in a high-speed mixer/granulator.

The high-speed mixer/granulator, also known as a high-speed mixer/densifier, may be a batch machine such as the Fukae (Trade Mark) FS, or a continuous machine such as the Lödige (Trade Mark) Recycler CB30. Suitable processes are described, for example, in EP 340 013A, EP 367 339A, EP 390 251A, EP 420 417A and EP 506 184A (Unilever).

One suitable method comprises spray-drying a slurry of compatible heat-insensitive ingredients, including zeolite and any other builders, and at least part of the detergent-active compounds: densifying the resulting base powder in a batch or continuous high-speed mixer/granulator; and then spraying on or postdosing those ingredients, for example, bleach, enzymes, unsuitable for processing via the slurry.

In another method, the spray-drying step can be omitted altogether, a high bulk density base powder being prepared directly from its constituent raw materials, by mixing and granulating in a high-speed mixer/granulator, and then postdosing bleach and other ingredients as in the spray-drying/post-tower densification route.

Generally the inorganic builders and other inorganic materials (for example, zeolite, sodium carbonate) are granulated with the surfactants, which act as binders and granulating or agglomerating agents. Where an anionic surfactant such as PAS is present, a mobile surfactant blend as described in EP 265 203A (Unilever) or EP 507 402A (Unilever) may suitably be used. Any optional ingredients as previously mentioned may be incorporated at any suitable stage in the process. In accordance with normal detergent powder

SUBSTITUTE SHEET

manufacturing practice, bleach ingredients (bleaches, bleach precursor, bleach stabilisers), proteolytic and lipolytic enzymes, coloured speckles, perfumes and foam control granules are most suitably admixed (postdosed) to the dense granular product after it has left the high-speed mixer/granulator.

The low-ethoxylated highly branched nonionic surfactants with which the present invention is concerned will not normally be included in the base powder but will be admixed with, for example, sprayed onto, the finished base powder. Nonionic surfactants of higher ethoxylation may be included in the base powder, post-added, or both. Preferably at least a part of any higher-ethoxylated nonionic surfactant is included in the base powder, while either low-ethoxylated surfactant alone or a mixture of higher- and low-ethoxylated nonionic surfactant is post-added.

EXAMPLES

The following non-limiting Examples illustrate the invention. Examples identified by numbers are in accordance with the invention, those identified by letters are comparative. Parts and percentages are by weight unless otherwise stated.

Examples 1 and 2, Comparative Examples A and B

Particulate detergent compositions were prepared by spray-drying aqueous slurries to form base powders (including nonionic surfactants as specified), densifying the base powder in a continuous Lödige high-speed mixer/granulator, spraying on further nonionic surfactants as specified, and then admixing the remaining ingredients.

- 19 -

The general formulation in weight percent is shown in Table 3.

TABLE 3

<u>Base powder</u>		
5	Linear alkylbenzene sulphonate	8.60
	*Nonionic surfactant (i)	1.92
	Zeolite 4A ¹	23.61
	Acrylic/maleic copolymer ²	3.51
	Sodium carbonate	7.49
10	Minor ingredients ³	1.35
	Moisture	9.02

		55.50
<u>Sprayed on</u>		
15	**Nonionic surfactant (ii)	4.68
<u>Admixed</u>		
	Zeolite 4A	5.00
	Sodium carbonate	4.30
	Granular sodium silicate	3.75
20	TAED ⁴	7.75
	Sodium perborate monohydrate	15.00
	EDTMP ⁵	0.37
	Antifoam granules ⁶	2.00
	Enzyme granules	1.00
25	Perfume	0.65

		100.00

*specified below

**specified below: when mixtures of two nonionic surfactants was used, they were in equal proportions (2.34 wt% each).

SUBSTITUTE SHEET

¹Wessalith (Trade Mark) P powder ex Degussa: percentage is for anhydrous material, the water of hydration being included in the figure for total moisture.

²Sokalan (Trade Mark) CP5 ex BASF.

5 ³Fluorescer, sodium carboxymethylcellulose, salts, etc.

⁴Tetraacetylenehydrazine, as 83 wt% granules.

⁵Ethylenediaminetetramethylenephosphonic acid, calcium salt: Dequest (Trade Mark) 2047 ex Monsanto (34 wt% active).

⁶Antifoam granules in accordance with EP 266 863B (Unilever).

10 The powders had bulk densities above 700 g/litre.

 The nonionic surfactants used were as shown in Table 4. Details of all these materials are given earlier in this specification.

- 21 -

TABLE 4

<u>Example</u>		<u>Surfactant (i)</u> (base powder)	<u>Surfactant (ii)</u> (sprayed on)
5	A	Synperonic A7	Synperonic A3 Synperonic A7
	B	Synperonic A7	Synperonic A3
	C	Synperonic A7	Dobanol 25-3
	D	Lialet 125-7	Synperonic A3 Synperonic A7
10	1	Synperonic A7	Lialet 125-3
	2	Synperonic A7	Genapol GX-030
	3	Synperonic A7	Lialet 111-3
	4	Synperonic A7	Lialet 111-3 Lialet 111-7
15	5	Lialet 125-7	Lialet 125-3
	6	Lialet 125-7	Lialet 125-3 Lialet 125-7

The powders were compared using two different tests.

SUBSTITUTE SHEET

Test 1

Delivery characteristics of the powders were compared using a model system which emulates the delivery of a powder in an automatic washing machine from a flexible delivery
5 device of the type supplied with Lever's Persil (Trade Mark) Micro System powder in the UK: a spherical container of flexible plastics material having a diameter of approximately 4 cm and a top opening of diameter approximately 3 cm.

In this test the delivery device was attached in an
10 upright position (opening uppermost) to an agitator arm positioned above water. By means of this apparatus the device could be moved vertically up and down through a distance of 30 cm, the lowest 5 cm of this travel being under water. Each up or down journey had a duration of 2 seconds,
15 the device being allowed to rest 5 cm under water for 4 seconds at the lowest position, and at the highest position being rotated through 100° and allowed to rest in the resulting tilted orientation for 2 seconds before redescending. 5 litres of water at a temperature of 20°C
20 were used.

A preweighed powder sample was introduced into the device in its highest position, and the apparatus then allowed to operate for six cycles and stopped when the device was again in its highest position. Surface water was carefully poured
25 off, and any powder residues transferred to a preweighed container. The container was then dried at 100°C for 24 hours, and the weight of dried residue as a percentage of the initial powder weight calculated.

The results are shown in Table 5.

- 23 -

TABLE 5

<u>Example</u>	<u>Surfactant (i)</u> (base powder)	<u>Surfactant (ii)</u> (sprayed on)	<u>Residue</u> (wt%)
5 A	Synperonic A7	Synperonic A3 Synperonic A7	52
B	Synperonic A7	Synperonic A3	75
1	Synperonic A7	Lialet 125-3	0

Test 2

10 The powders were also compared by means of a washing machine test. The machine used was a Siemens Siwamat (Trade Mark) Plus 3700 front-loading automatic washer and the test methodology was as follows.

15 A 100 g dose of powder was placed in a flexible delivery device as described previously. The delivery device was placed inside a black cotton pillowcase having dimensions of 30 cm by 60 cm, taking care to keep it upright, and the pillowcase was then closed by means of a zip fastener. The pillowcase containing the (upright) delivery device was then placed on top of a 3.5 kg dry cotton washload in the drum of
20 the washing machine.

SUBSTITUTE SHEET

The machine was operated on the "heavy duty cycle" at a wash temperature of 60°C, using water of 15° French hardness and an inlet temperature of 20°C.

At the end of the wash cycle the pillowcase was removed,
5 opened and turned inside out, and the level of powder residues on its inside surfaces determined by visual assessment using a scoring system of 1 to 3: a score of 3 corresponds to a residue of approximately 75 wt% of the powder, while 1 indicates no residue. A panel of five assessors was used to
10 judge each pillowcase and allot a score. With each powder the wash process was carried out ten times and the scores were averaged over the ten repeats.

The results were as shown in Table 6.

- 25 -

TABLE 6

	<u>Example</u>	<u>Surfactant (i)</u> (base powder)	<u>Surfactant (ii)</u> (sprayed on)	<u>Score</u>
5	A	Synperonic A7	Synperonic A3 Synperonic A7	2.6
	B	Synperonic A7	Synperonic A3	3.0
	C	Synperonic A7	Dobanol 25-3	2.9
	D	Lialet 125-7	Synperonic A3 Synperonic A7	2.5
10	1	Synperonic A7	Lialet 125-3	1.4
	2	Synperonic A7	Genapol GX-030	1.5
	3	Synperonic A7	Lialet 111-3	1.3
	4	Synperonic A7	Lialet 111-3 Lialet 111-7	2.2
15	5	Lialet 125-7	Lialet 125-3	1.6
	6	Lialet 125-7	Lialet 125-3 Lialet 125-7	2.3

SUBSTITUTE SHEET

Detergency

A washing machine test was also carried out to compare the detergencies of the compositions of Examples A, B, C (comparative) and 1 and 2 (in accordance with the invention).

- 5 The machine was again a Siemens Siwamat. 3 kg loads containing WFK-10C test cloth monitors (cotton soiled with a mixed fatty and particulate soil: wool fat and kaolin) were washed at 20°C using the half load main wash cycle. The powder samples (80 g dose) were introduced via the machine's
10 dispenser. Detergency results (reflectance increases at 460 nm of the test cloth monitors) were as follows:

<u>Example</u>	<u>Reflectance increase</u>
A	7.1
B	5.6
15 C	8.0
1	15.3
2	13.9

These results demonstrate the additional benefit associated with the invention, of improved detergency.

- 27 -

Example 7, Comparative Example E

In this Example the dispersability of high bulk density base powders containing different nonionic surfactants was compared in a test designed to detect the formation of gel surfactant phases as the powder is wetted.

The powders were prepared as follows. In each case, the base powder was prepared by granulation with in-situ neutralisation in a high-speed mixer/granulator, as described in EP 420 417A and EP 506 184A (Unilever), and the remaining ingredients were then admixed. The finished powders had bulk densities in the 800-900 g/l range.

The formulations (in parts by weight) were as follows:

		<u>E</u>	<u>Z</u>
	CocoPAS	6.51	6.51
15	Nonionic surfactant:		
	Lorodac 7	6.48	-
	Lorodac 3	8.19	-
	Lialet 111-7	-	6.48
	Lialet 111-3	-	8.19
20	Soap	2.26	2.26
	Zeolite MAP (hydr)	41.74	41.74
	Carbonate	1.11	1.11
	SCMC	1.02	1.02

SUBSTITUTE SHEET

The nonionic surfactants were as follows:

<u>Ex.</u>	<u>Nonionic</u>	<u>Chain length</u>	<u>Branching</u>	<u>EO</u>
E	Lorodac 7	coconut (C ₁₂₋₁₆)	none	7EO
	Lorodac 3	coconut (C ₁₂₋₁₆)	none	3EO
5 7	Lialet 111-7	C ₁₁	47% (C ₁₋₄)	7EO
	Lialet 111-3	C ₁₁	47% (C ₁₋₄)	3EO

The dispersion test was carried out as follows. An
0.3 g sample of powder was placed in a small spoon and wetted
by holding the spoon horizontally in water at 10°C for 1
10 minute. The spoon was then removed and surplus water poured
off. The spoon with the damp powder was then placed
horizontally in a 500 ml beaker of water at 10°C and a stirrer
(a magnetic flea set to give a 25 mm vortex) was activated.
Turbidity (as indicator of the dispersion of the zeolite) was
15 measured as a function of time.

The 90% dispersion times were as follows:

Comparative Example E	4.50 minutes
Example 7	1.66 minutes

- 29 -

Examples 8 and 9, Comparative Examples F and G

In these Examples, the oily soil detergencies (percentage removal of radio-labelled triolein soil from polyester) of surfactant systems containing cocoPAS (30 parts) and different nonionic surfactants (70 parts) having similar degrees of ethoxylation were compared in the tergotometer using a 5 g/l product concentration, 24^o (French) hard water, and a wash temperature of 20^oC.

Compositions were prepared to the following general formulation, nonionic surfactants and detergencies being shown in the table below:

	<u>parts</u>	<u>%</u>
cocoPAS	5.10	6.71
Nonionic surfactant (see below)	11.90	15.66
15 Zeolite 4A	32.0	42.11
Carbonate	10.0	13.16
Silicate	0.5	0.66
Metaborate	16.5	21.70
	----	-----
20	<u>76.0</u>	<u>100.00</u>

<u>Ex.</u>	<u>Nonionic surfactant</u>	<u>Chain length</u>	<u>Branching</u>	<u>EO</u>	<u>Detergency</u>
F	Dobanol 91-5	C ₉₋₁₁	16%	5.0	12.4
8	Lialet 111-4	C ₁₁	47%	4.0	27.1
25 9	Lialet 111-5	C ₁₁	47%	5.0	27.1
G	Coco 7EO/ coco 3EO (30/40)	C ₁₂₋₁₄	none	4.5-5	23.3

SUBSTITUTE SHEET

Examples 10 and 11, Comparative Examples H and J

The procedure of Examples 8, 9, F and G was repeated using compositions in which the surfactant systems each consisted of 10 parts of cocoPAS and 90 parts of ethoxylated nonionic surfactant.

Compositions were prepared to the following general formulation, nonionic surfactants and detergencies being shown in the table below:

		<u>parts</u>	<u>%</u>
10	cocoPAS	1.70	2.24
	Nonionic surfactant (see below)	15.30	20.13
	Zeolite 4A	32.0	42.11
	Carbonate	10.0	13.16
	Silicate	0.5	0.66
15	Metaborate	16.5	21.70
		----	-----
		<u>76.0</u>	<u>100.00</u>

<u>Ex.</u>	<u>Nonionic</u> <u>surfactant</u>	<u>Chain</u> <u>length</u>	<u>Branching</u>	<u>EO</u>	<u>Detergency</u>
20	F Dobanol 91-5	C ₉₋₁₁	16%	5.0	33.5
8	Lialet 111-4	C ₁₁	47% (C ₁₋₄)	4.0	41.7
9	Lialet 111-5	C ₁₁	47% (C ₁₋₄)	5.0	37.8
G	Coco 7EO/ coco 3EO (30/40)	C ₁₂₋₁₄	none	4.5-5	36.1

*

*

*

- 31 -

CLAIMS

- 1 A particulate detergent composition having a bulk density
of at least 600 g/l and comprising a surfactant system
comprising a nonionic surfactant, at least one detergency
5 builder and optionally other detergent ingredients, wherein
the nonionic surfactant comprises a branched-chain nonionic
surfactant which is an ethoxylated C₈-C₁₅ aliphatic alcohol
having a degree of chain branching (defined herein as the
weight% of the alcohol constituted by branched material) of at
10 least 40 wt%, and having an average degree of ethoxylation of
from 2 to 6, and the surfactant system is substantially free
of ethoxylated alcohol nonionic surfactants having a degree of
chain branching of less than 40 wt% and a degree of
ethoxylation of from 2 to 6.
- 15 2 A detergent composition as claimed in claim 1, wherein
the branched-chain nonionic surfactant has a degree of chain
branching of from 45 to 70 wt%.
- 3 A detergent composition as claimed in claim 1, wherein
the branched-chain nonionic surfactant has a degree of chain
20 branching of at least 50 wt%.
- 4 A detergent composition as claimed in claim 1, wherein
the branched-chain nonionic surfactant has an average degree
of ethoxylation of from 2.5 to 4.

SUBSTITUTE SHEET

5 A detergent composition as claimed in any preceding
claim, wherein the surfactant system also comprises a further
nonionic surfactant which is a condensation product of
ethylene oxide with a C₈-C₁₅ aliphatic alcohol having an
5 average degree of ethoxylation within the range of from 6.5 to
10.

6 A detergent composition as claimed in claim 5, wherein
the further nonionic surfactant has a degree of ethoxylation
within the range of from 6.5 to 8.

10 7 A detergent composition as claimed in claim 5 or claim 6,
wherein the further nonionic surfactant has a degree of chain
branching of less than 40 wt%.

8 A detergent composition as claimed in any preceding claim,
wherein the surfactant system further comprises anionic
15 surfactant.

9 A detergent composition as claimed in claim 8, wherein
the surfactant system consists essentially of linear
alkylbenzene sulphonate and/or primary alcohol sulphate, and
ethoxylated nonionic surfactant.

- 33 -

10 A detergent composition as claimed in claim 9, wherein the surfactant system consists essentially of

(i) from 40 to 100 wt% of ethoxylated nonionic surfactant, and

5 (ii) from 0 to 60 wt% of linear alkylbenzene sulphonate or primary C₈-C₁₈ alcohol sulphate.

11 A detergent composition as claimed in any preceding claim, which contains from 10 to 50 wt% of the surfactant system.

10 12 A detergent composition as claimed in any preceding claim, which comprises as detergency builder from 20 to 60 wt% (anhydrous basis) of alkali metal aluminosilicate.

13 A detergent composition as claimed in any preceding claim, having a bulk density of at least 700 g/l.

15 14 Use of a branched-chain nonionic surfactant which is an ethoxylated C₈-C₁₅ aliphatic alcohol having a degree of chain branching of at least 40 wt% (based on the alcohol) and having an average degree of ethoxylation of from 2 to 6, to improve the solubility and/or rate of dissolution of a particulate
20 detergent composition having a bulk density of at least 600 g/l.

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 93/02346

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11D17/06 C11D1/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Derwent Publications Ltd., London, GB; AN 89-066624 & JP,A,1 020 299 (KAO CORP.) 24 January 1989 see abstract</p>	1,8,9, 12,14
A	<p>FR,A,2 267 369 (PROCTER & GAMBLE) 7 November 1975 see claims</p>	1-10
A	<p>US,A,4 166 039 (R.M. WISE) 28 August 1979 see column 12, line 46 - column 13, line 51; claim 1; examples</p>	1,5,8,9, 12
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- '&' document member of the same patent family

Date of the actual completion of the international search

8 March 1994

Date of mailing of the international search report

18. 03. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 93/02346

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 339 672 (PROCTER & GAMBLE) 26 August 1977 see page 3, line 16 - line 40; claim 1 ---	1
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 92-014323 & JP,A,3 265 699 (LION CORP.) 26 November 1991 see abstract -----	1,8,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 93/02346

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
FR-A-2267369	07-11-75	GB-A-	1495145	14-12-77
		BE-A-	827780	10-10-75
		CA-A-	1050378	13-03-79
		DE-A, C	2514676	23-10-75
		JP-A-	51016304	09-02-76
		NL-A-	7504262	14-10-75

US-A-4166039	28-08-79	AU-A-	7429074	15-04-76
		BE-A-	821094	15-04-75
		CA-A-	1039141	26-09-78
		CH-A-	606416	31-10-78
		DE-A, C	2448502	24-04-75
		FR-A, B	2247530	09-05-75
		GB-A-	1460646	06-01-77
		JP-A-	50111108	01-09-75
		JP-B-	57030160	26-06-82
		NL-A-	7413521	17-04-75
		SE-A-	7412902	16-04-75

FR-A-2339672	26-08-77	BE-A-	851005	02-08-77
		CA-A-	1080576	01-07-80
		DE-A-	2703505	04-08-77
		GB-A-	1566326	30-04-80
		NL-A-	7701022	04-08-77
